Building the Foundation for the CropManage Nitrogen Fertilizer Decision Support Framework to Guide Hawaii's Vegetable Production Systems

A THESIS IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

TROPICAL PLANT AND SOIL SCIENCES
UNIVERSITY OF HAWAI'I AT MĀNOA

NOVEMBER 2016

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Acknowledgements

This research was made possible through the help and support of many others and I would like to acknowledge all of the people who assisted me throughout this project as well as throughout the course of my degree. I feel truly blessed to have had the opportunity to contribute to such a meaningful project and I thank my principle advisor Dr. Jonathan Deenik for brining me on board as his graduate student.

First I would like to give my most sincere gratitude to my committee members, Dr. Deenik, Dr. Yost, and Dr. Ryals. For it was through your unwavering support and words of encouragement that kept me on track and allowed me to succeed. Thank you all for remaining committed to me through the good times and the rough times, it was pleasure having each of you on my committee.

Next I would like to extend my deepest thanks to Jensen Uyeda, extension agent with the College of Tropical Agriculture and Human Resources who played an instrumental role in making this project a reality. Thank you for working relentlessly in obtaining project funding, recruiting cooperating farmers, and involving CTAHR extension services to help me with data collection activities.

I would like to extend a special thanks to Dr. Michael Cahn at the University of California Davis for his technical guidance with the overall project. Thank you for your willingness to collaborate and share all of the proprietary knowledge and experience that you've acquired during your development of CropManage.

I like to give a big mahalo, to the many individuals who help me collect data and analyze samples. Thanks to CTAHR extension agents Jensen Uyeda, Josh Silva, Steve Fukuda, Kylie Wong, and Fred Reppun for their assistance with field work. Thanks to Dr. Susan Crow and her entire lab especially Jon Wells, Christine Glazer and Lauren Deem for technical assistance running analytical equipment. Thanks to the many student workers and volunteers who help me in the field, Elia Bruno, Kristy Lam, Ryan Hodges, Tiziana Ruiz, David Hodges, Zach Gebhard, Erika Pauley, Antonio Rocha, Tiare Silvasy, Amber Au, Yu-Fen Huang, and Connor Palmer for assistance in laboratory and field work. Thanks to the Poamoho Research Station crew for assistance throughout my experiment at the research station.

Finally, thank you to the TPSS ohana for all the unconditional support and much thanks to my family and close friends whom supported and encouraged me throughout my degree.

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Chapter One

Introduction

As population growth continues on its current trajectory, the agricultural production necessary to support this rapid expansion is posing immense threats to the environment (Galloway et al., 2008; Vitousek et al., 1997). Nitrogen (N) nutrition is one of the most critical aspects of food production as proper N management is fundamental to crop growth while improper N management adversely affects environmental health. There is evidence of a global nitrogen dilemma (Foley et al., 2011). There are two extreme scenarios at play in regards to the global nitrogen dilemma: an unfortunate and dire lack of sufficient N resources to support crop production that meets basic caloric demands in the developing world (Sanchez, 2002; Sanchez and Swaminathan, 2005), and at the other extreme, the developed world, that has grown accustomed to convenient diets based on high N fertilizer from Haber-Bosch processes to create food surpluses as well as associated environmental problems (Galloway et al., 2008). The latter scenario poses catastrophic global consequences if kept on its current trajectory.

The catastrophe is rooted in the adverse environmental effects of excess reactive N. The term reactive nitrogen (Nr) is defined as all biologically active, photochemically reactive, and radiatively active N compounds in the atmosphere and biosphere (Galloway et al., 2008). Release of Nr into the environment from human activities poses threats to human and ecosystem health on both regional and global scales (Foley et al., 2005; Rockstrom et al., 2009; Socolow, 1999; Tilman, 1999). Since the industrial revolution, human activities have more than doubled the global pool of Nr from inert pools (Vitousek et al., 1997). Fertilizer N is the dominant force driving the increases of Nr out of all anthropogenic sources (Socolow, 1999). The trends in N fertilizer production and consumption show that global N fertilizer use has risen by an order of magnitude from 1960 until 2005 going from 1 million tons to 9.8 million tons respectively (Keeney and Hatfield, 2008) and has yet to reach an asymptote (Conant et al., 2013; Galloway et al., 2008).

To avert catastrophe, greater emphasis must be placed on developing N fertilizer strategies that mitigate the release of Nr into the environment for both large and small scale farming systems alike.

In Hawaii, over a hundred years of large scale sugarcane and pineapple agriculture depended on large inputs of fertilizer N (Bartholomew et al., 2002; Humbert, 2013; Silva and Uchida, 2000). During the plantation era, N fertilizer rates as high as 420 kg ha^{-1} for sugar cane (Humbert, 2013) and rates in excess of 400 - 500 kg ha^{-1} for pineapple were applied to vast stretches of land (Bartholomew et al., 2002). In the last 38 years (1980 to 2018) Hawaii's agricultural landscape has experienced a massive shift away from centralized plantations to small farms with a greater diversity in crops. From the year 1980 to 2018 land under the cultivation of sugarcane and pineapple reduced from 300,000 to 4,500 acres. In the same time frame, land under cultivation of diversified crops expanded from 7,500 to 17,000 acres (Melrose et al., 2015). These drastic changes in agricultural land use have resulted in a net reduction of area under cultivation. However, despite an overall reduction in cultivated area, certain key changes in land management will continue the potential for negative environmental impacts due to mismanagement of N fertilizer (Ling, 1996; Silva and Uchida, 2000). Moreover, the growing number of individual diversified farmers with a range of farming systems necessitates the need for adaptive N management strategies. For example, increasing numbers of intensive farming systems may choose to grow more crops annually, at a higher planting density. Such choices would increase the use of N fertilizer and if applied in excess, leach more nitrates into fresh water aquifers and aquatic ecosystems. In Hawaii, there is a need for a logical scientific approach to N fertilizer management that better matches fertilizer N application to crop N requirements.

As Hawaii moves on from the plantation era with the intent to increase vegetable crop production for local markets, awareness of N pollution and willingness to adopt proper N management strategies is paramount. However, adoption of N management strategies is not a simple process and Hawaii faces several fundamental challenges, which make development and widespread adoption difficult. Of paramount importance is the diversity of topography and its effects on creating a great diversity of microclimates and soil types with widely varying chemical

and physical properties (Deenik and McClellan, 2007; Ikawa et al., 1985; Uehara, 1994). Climate and soil diversity make development and implementation of universal N management practices very difficult. In Hawaii it is wise to develop site, crop, and soil specific N management strategies for the many different microclimates and soil types.

Historically, two general approaches exist to guide N fertilizer recommendations. One is through fertilizer response curves in which either a maximum marketable yield or maximum economic return to nitrogen is determined (Burns, 2004; Morris et al., 2017; Silva et al., 2000). The second is through the use of an N balance equation in which a crop N requirement is determined and the N fertilizer recommendation is the difference between the crop N requirement and the soil N supply (Morris et al., 2017; Stanford, 1973). Both methods serve as a framework to developing N fertilizer recommendations and both have their sets of strengths and weaknesses.

Fertilizer response curves developed through field experiments provide an N rate for a maximum marketable yield. Fertilizer response curves can also provide an N rate for maximum economic return to applied nitrogen, which is identified based on the price of N fertilizer and the price of the crop commodity (Burns, 2004). However, there are two major weaknesses to this approach: first, fertilizer response curves do not account for soil N pools that can contribute to crop N uptake increasing potential for excess N with economic and environmental consequences, and second, there is a low certainty of choosing the correct N rate for a given field in a given year due to large variability's in temporal and spatial factors that influence yield response to N fertilizer (Morris et al., 2017). To overcome the limitations of the fertilizer response approach, the N balance equation is the framework that most N management approaches have been based on in the US from 1970's to 2005 (Morris et al., 2018). The logic for the N balance equation was first laid out by Stanford (1973). The N balance approach requires accurate estimates for total quantity of N required for the crops to complete its production cycle (N_y) minus the contribution of soil N supply (N_s). The difference between N_y and N_s is then divided by the efficiency in which applied N will be taken up by the crop (E_f). The basic formula proposed to calculate N fertilizer recommendations takes the general form:

$$N_f = \frac{(N_y - N_s)}{E_f} \qquad \text{[EQN 1.1]}$$

Where, N_f= the amount of N that must be supplied as fertilizer, N_y= the total quantity of N a crop must accumulate to complete its production cycle, N_s= is the contribution of soil N in the total N supply to the crop, and E_f= a decimal value that represents the crop N recovery efficiency.

There are four general fertilizer recommendation approaches that are derived from the N balance equation. The four approaches are; look-up tables that utilizes soil indices to determine soil N supply (Rahn et al., 1998); soil mineral nitrogen method that uses measured SMN to determine soil N supply (Fink and Scharpf, 1993); N balance sheet method which consists of many iterations of (EQN 1.1) that include additional factors which account for specific soil, crop, environment, and management factors that influence the overall N fertilizer recommendation (Morris et al., 2017); and simulation models of crop N response that can solve a series of N balance equations for each successive day throughout the crop duration (Li, 1997).

More recently, web-based software tools have been developed to guide in-season N fertilizer application and scheduling. CropManage is a web based irrigation and N fertilizer management platform that utilizes crop growth models, real time weather data, and user inputs such as measured soil nitrate concentrations to make precise in-season N fertilizer recommendations (Cahn et al., 2015). The N fertilizer component of CropManage is based on a simplified version of the N-balance equation (EQN 1.2). The primary parameter inputs include; annual crop N accumulation (N_y), pre-plant estimates of soil NO_3-N ha^{-1} (N_{SIN}), estimates of previous crop residue N ha^{-1} as an N credit (N_{CRN}), and estimates of easily mineralizable soil organic nitrogen as an N credit (N_{SON}). CropManage also utilizes models of crop N uptake dynamics in conjunction with a pre-sideress soil nitrate quick test (SNQT) to further synchronize N fertilizer timing with crop N uptake. (EQN 1.2).

$$N_f = \frac{(N_y - N_{SIN} - N_{SON} - N_{CRN})}{E_f} \quad \text{[EQN 1.2]}$$

Where, N_f= the amount of N that must be supplied as fertilizer throughout the crop growth cycle, N_y= the total quantity of N a crop must accumulate to complete its production cycle, N_{SIN}= the measurement of soil mineral nitrogen that is available to the crop, N_{SON}= the estimate of soil organic nitrogen that will mineralize and become available to the crop, N_{CRN}= is the amount of N

in crop residue that will be returned to the soil as an N credit, and E_f = a decimal value that represents the crop N recovery efficiency.

This slightly expanded equation provides a good starting point for seasonal N fertilizer recommendations. However, it is a static approach that fails to capture the temporal dynamics of the soil/crop system throughout the growing season (Lory and Scharf, 2003). In other words, the N balance equation above is a model that looks at N requirement of an entire cropping season without accounting for in-season variation in soil N status or weather events such as storms that will affect soil N status. To addresses the drawbacks to the static nature of the N balance equation, CropManage incorporates site and crop specific N uptake dynamics, pre-sidedress soil nitrate quick tests (SNQT) and a triangulation of historical weather patterns with real time weather data, to account for in-season variability and further synchronize N fertilizer timing with crop N uptake.

This study focused on developing a diagnostic tool to rapidly assess soil nitrate status to support the use of an N balance approach to N fertilizer recommendation. My contribution represents one component of a bigger project that involves adapting the CropManage, a web-based N fertilizer and irrigation scheduling software tool (Cahn et al., 2015), to Hawaii farming systems. The CropManage N recommendation procedure utilizes an N balance approach (EQN 1.1) combined with an in-field soil nitrate quick test. The overall goal of the project is to apply an N balance approach to fertilizer recommendations for intensive vegetable production systems in Hawaii, with a focus on developing a diagnostic tool to assess soil nitrate status. The SNQT is a valuable diagnostic tool that can help farmers rapidly assess soil nitrate status to better synchronize N applications with N uptake patterns of their crops. To encourage wide spread adoption of the SNQT our specific objectives of this study were to:

1) Evaluate the accuracy of the SNQT in a wide range of Hawaii soils.
2) To develop SNQT critical concentrations for a brassica crop grown on an important Oxisol.

Chapter Two

Assessment of the Pre-sidedress Soil Nitrate Quick Test Diagnostic Value in Hawaii Vegetable Systems

Abstract

There is a need for nitrogen (N) fertilizer management strategies that can improve synchrony between N fertilizer application and crop N uptake in Hawaii. The ability to diagnose soil mineral nitrogen (SMN) status in a timely fashion can facilitate farmer adoption of N fertilizer management strategies. Although soil N diagnostic technology has been available for about four decades, there are critical drawbacks to the standard testing procedure that discourages farmer adoption of such tests. Recent developments of an on-farm soil testing methodology referred to as the soil nitrate quick test (SNQT) have shown great promise in overcoming the drawbacks associated with standard testing procedures. The proper steps needed to encourage widespread adoption of on-farm soil testing technology include accuracy assessment across regional soil types as well as crop and site specific calibration. We assessed the accuracy of the SNQT in agricultural soils throughout Hawaii, across a diversity of soil types as well as a wide range of soil nitrate concentrations. We also calibrated the SNQT on a Rhodic Haplustox for napa cabbage (*Brassica rapa subsp. pekinensis*) by identifying soil nitrate-N (NO_3-N) critical concentrations beyond which response to N fertilizer is unlikely. The results indicate that the SNQT provides an acceptable estimation of soil NO_3-N concentration that is similar to results using the standard soil testing methodology (r^2 =0.95). We also propose an SNQT critical concentration for napa cabbage of 38 mg kg^{-1} NO_3-N when the test was used as a pre-sidedress soil test (PSNT) two weeks after planting. Overall evaluation of the SNQT indicates that the test is a suitable diagnostic tool for Hawaii farmers.

Introduction

Large inputs of nitrogen (N) fertilizers have been associated with profitable crop production in major agricultural regions of the United States (Yadav et al., 1997). Such practices

have been commonly recommended in Hawaii's commercial agriculture industry (Hue et al., 2004). However, large applications and associated losses from the farm can adversely affect the environment (Galloway et al., 2003). Studies in Hawaii have demonstrated the potential for N fertilizers to escape the farm system through leaching or run-off and directly degrade local ground water supplies and marine ecosystems. The use of groundwater geochemical modeling combined with stable isotope analysis has enabled scientists to connect land-use practices and groundwater flow paths with unhealthy nutrient fluxes to the ocean (Fackrell et al., 2016). Furthermore, recent research in Hawaii has confirmed that commercial agricultural activities have had substantial negative impacts on costal ecosystems (Bishop et al., 2017). Researchers in Hawaii have also estimated N leaching rates into fresh water aquifers as high as 200 kg N $ha^{-1}yr^{-1}$ (Reinhart, 2001).

Because N can be lost through many pathways, the soil-crop system is notoriously difficult to manage in soils and environments of tropical regions (Ewel, 1986). Efficient management of N fertilizers is difficult to achieve, in part, because of the complexities of the N cycle and the many pathways for N transformation. Nitrogen use efficiency (NUE), defined as the percent of crop uptake derived from soil N and fertilizer N (Kitchen et al., 2008), is typically less than 50% worldwide (Fageria and Baligar, 2005). The primary loss pathways that decrease NUE are nitrate leaching, denitrification, and ammonia volatilization (Cassman et al., 2002). Efforts have been made to increase NUE in major vegetable and grain producing regions of the US due to concerns over adverse environmental and human health impacts and pressure from regulatory agencies (Bottoms et al., 2012; Guillard et al., 1999). In Hawaii increased efforts by farmers, institutions, and policymakers must be directed towards development and use of N management practices shown to increase NUE.

One N management strategy with potential to improve NUE uses a mass balance approach within the soil-crop system (Stanford, 1973). Plants have an internal N demand that is correlated to target yields, which must be met by plant-available N supplied by the soil. However, in sustained cropping systems, the soil supplying capacity is usually insufficient to meet crop demands (Kitchen et al., 2008). This deficit must be met through the application of N fertilizer.

The amount of N fertilizer needed can be calculated from data quantifying the different components in the soil plant system. Specifically, estimates for optimum N fertilizer requires three components: the amount of mineral N present in the soil, the amount of N that will likely mineralize from the pool of soil organic nitrogen (SON) during crop growth, and the amount of N the crop will need to meet a target yield. With estimates of these three components, the quantity of N fertilizer can be calculated. Using these specific data the equation to compute a fertilizer recommendation is referred to as an N balance equation.

$$N_f = \frac{(N_y - N_s)}{E_f} \quad \text{[EQN 2.1]}$$

Where, N_f = the amount of N that must be supplied as fertilizer throughout the crop growth cycle, N_y = the total quantity of N a crop must accumulate to complete its production cycle, N_s = is the contribution of soil N in the total N supply to the crop, and E_f = a decimal value that represents the crop N recovery efficiency.

Determination of plant-available SMN is an analytical procedure that can provide useful information for N fertilizer decision makers. A SMN test or inorganic N soil test refers to measurements of nitrate-N (NO_3-N) and sometimes ammonium-N (NH_4-N). In most arable soils, oxidizing conditions facilitate the nitrification of ammonium (NH_4^+) to nitrate (NO_3^-), which can accumulate (Strawn et al., 2015). Consequently, soil NO_3-N tests often serve as the most useful measure of available SMN (Maynard et al., 2007).

Soil nitrate diagnostic technologies have existed for decades and there is great diversity in testing methods consisting of different extractions as well as determination techniques (Maynard et al., 2007; Mulvaney, 1996). The standard and most widely accepted method for soil NO_3-N analysis involves an extraction in 2 *M* KCl followed by spectrophotometric determination using an automated flow system (Maynard et al., 2007; Saha et al., 2018). The benefits of using this testing method include high precision with an applicable detection range of 0.01 to 2.0 mg N L^{-1}, as well as good accuracy and repeatability. The main drawbacks to this method include high cost per sample, long turnaround time, as well as the use of potentially caustic and carcinogenic reagents (Schmidhalter, 2005).

In Hawaii, there are two institutionalized diagnostic laboratories with the ability to conduct soil NO_3-N tests using standard laboratory methods of analysis. However, Hawaii vegetable farmers are reluctant to use soil tests to guide N fertilizer decisions for several reasons. First, the cost per sample is high and coupled with the time and labor required to sample, prepare, and transport the soil, the use of soil NO_3-N tests becomes less feasible than simply adding extra N fertilizer to insure no crop N deficiencies. Additionally, the time from sample collection to receiving soil test results is typically a week or longer which is unacceptable to farmers in Hawaii. In Hawaii's tropical climate with many potential N loss pathways, delayed receipt of data can be problematic (Hartz et al., 2000; Hue et al., 2004).

The soil nitrate quick test (SNQT) is an onsite soil testing protocol with the potential to overcome the main drawbacks preventing farmers from utilizing soil N testing to guide fertilizer application (Hartz et al., 2000). The SNQT involves an on-farm extraction of soil NO_3-N in 0.01 M $CaCl_2$ and immediate determination using nitrate sensitive colorimetric test strips. The practical utility of the SNQT depends on its rapidity, accuracy and diagnostic capabilities. There exists considerable research over the past four decades assessing the accuracy of the colorimetric strip test technology. Numerous soil test assessment studies report that the SNQT is accurate. (Schaefer, 1986) reported that the SNQT read by eye was highly correlated ($r^2 = 0.97$) with a laboratory ion chromatography method. Jemison and Fox (Jemison Jr and Fox, 1988) reported that the SNQT was highly correlated ($r^2 = 0.98$) with results of a laboratory electrode method. More recently, accuracy studies have been conducted comparing test results from the SNQT to results obtained by different established standard laboratory methods. A series of studies observed that the SNQT was highly correlated ($r^2 = 0.94$, 0.96, and 0.92) to measures obtained with the diffusion conductivity method (Breschini and Hartz, 2002; Hartz, 1994; Hartz et al., 2000) and Schmidhalter (2005) reported that the SNQT was highly correlated ($r^2 = 0.96$) with the ion chromatography method. However, no studies of this nature have been conducted with soils from tropical regions. Hawaii has a diversity of tropical soils and transfer of analytical technology across soil types is not a trivial process (Uehara and Gillman, 1981)There is a need to conduct

studies in Hawaii to verify the accuracy of the SNQT across the range of Hawaiian agricultural soils.

One of the main benefits of the SNQT is its diagnosis of soil N deficiency/sufficiency in a field setting. The SNQT can be used as a pre-plant soil nitrate test (PPNT) as well as an in-season pre-sidedress soil nitrate test (PSNT) to help farmers identify sites unlikely to respond to fertilizer additions (Hartz et al., 2000). When used as a pre-plant soil test, the SNQT can help a farmer identify sites where residual soil NO_3-N may contribute important amounts of available N to subsequent crops. When used as an in-season soil test, the SNQT can guide N fertilizer application timing to increase the synchrony between N fertilizer applied and crop N uptake.

In-season SNQT critical concentrations have been determined for various crops in different regions for practical use as a diagnostic indicator. The critical concentration represents a threshold value beyond which further additions of N fertilizer does not increase overall crop yields. Critical soil NO_3-N concentration for in-season use of the SNQT have been reported at 20-25 mg kg^{-1} across a range of soil types for sweetcorn (Heckman et al., 1995), fall cabbage (Heckman et al., 2002), tomatoes (Krusekopf et al., 2002), lettuce and celery (Hartz et al. 2000).The major benefit of using the SNQT methodology is its ability to produce timely on-farm estimates of soil NO_3-N at a relatively low cost (Breschini and Hartz, 2002). By simplifying the analytical steps of the process, test results can be made immediately available to a grower in time to guide in-season fertilizer applications.

The goal of this study was to improve N fertilizer management in Hawaii's diversified vegetable production systems. The overall objective of the research discussed in this chapter was to evaluate the SNQT method and validate it as a useful and applicable tool for Hawaii growers. The specific objectives of this study were to:

1) Assess the accuracy of the SNQT methodology relative to a standard laboratory method in a wide range of agriculturally important Hawaiian soil types;
2) Develop empirical soil moisture correction factors for quick interpretation of test strip results, and

3) Establish crop specific target yields based on SNQT critical NO_3-N concentrations for napa cabbage (*Brassica rapa subsp. pekinensis var.Yuki F1 hybrid*) grown in an Rhodic Haplustox.

Materials and Methods

SNQT accuracy assessment

We evaluated the accuracy of the SNQT by comparing NO_3-N readings determined by the SNQT with NO_3-N estimates obtained by the standard spectrophotometric laboratory method using an automated flow system (Maynard et al., 2007; Mulvaney, 1996).

A total of 73 soil samples used for the assessment were collected from two separate and independent studies. Eighteen of the soil samples were collected from various farms, research centers, and pasture areas throughout the islands of Hawaii, Maui, and Oahu. The eighteen soil samples encompassed a range of soil types (Table 2.1) that were used for a long-term N mineralization study. Additional 55 soil samples were collected during a research study in which soil and crop N dynamics were modeled in response to typical commercial N fertilizer practices. In this assessment soil samples were collected weekly throughout the duration of head cabbage (*Brassica oleracea var.capitata*), napa cabbage (*Brassica rapa subsp. pekinensis var.Yuki F1 hybrid*), and broccoli (*Brassica oleracea* 'Calabrese') production. The soil in this particular sample set is classified as a Wahiawa silty clay (Very-fine, kaolinitic, isohyperthermic Rhodic Haplustox) (USDA 2016a). The soil samples encompassed a broad range of soil NO_3-N concentrations.

All samples were analyzed for NO_3-N concentration using the SNQT method and the standard laboratory procedure (Maynard et al., 2007). For the SNQT methodology, soil samples were analyzed using the procedure described by Hartz (2000). For this procedure, we measured a 10 mL volume of field moist soil into a 50 mL centrifuge tube containing 30mL of 0.01 *M* $CaCl_2$ extracting solution. The tubes were shaken by hand for 5 minutes following the recommended time needed to completely disperse soil aggregates in a fine textured clay soil (Schmidhalter, 2005). The extracts were then filtered through pre-leached Whatman # 42 filter paper and NO_3-N

concentrations were determined using nitrate test strips (Reflectoquant Nitrate Test, Cat. No. 1.16995.001, EMD Millipore Corporation, Billerica, MA) and a hand held reflectometer (Reflectometer RQflex plus, Cat. No. 1.16955.0001,EMD Millipore Corporation, Billerica, MA). In order to adjust soil NO_3-N readings to a dry soil basis, the dry soil weights of the field moist soil samples for each extraction were recorded. Gravimetric moisture content was determined on a subsample through mass balance by oven drying soil samples at 105°C to a constant weight.

The same soil samples used for the SNQT were analyzed for KCl-extractable NO_3-N following standard laboratory methodology using the procedure described by Maynard et al (2007). A 5 g field moist soil sample was extracted with 50 mL of 2*M* KCl in a 125ml Erlenmeyer flask. The samples were shaken on a conical shaker for 60 minutes at 160 strokes per minute. After shaking, extracts were filtered through pre-leached Whatman # 42 filter paper and NO_3-N concentrations by cadmium reduction were determined spectrophotometrically using an automated flow system (QuikChem® Method 12-107-04-1-F) (QuikChem 8500 Series Automated Ion Analyzer, Lechat Instruments, Loveland, Colorado). The NO_3-N concentrations were recorded on a dry soil basis by adjusting for gravimetric moisture content.

Soil NO_3-N extractions following standard laboratory methodologies recommend using 2M KCl as a standardized extractant. In laboratory settings it is common to have soil samples analyzed for NO_3-N and NH_4-N concurrently. NO_3-N is water-soluble thus can be extracted easily, however, NH_4-N is an exchangeable cation that is held to the soils negative charge and must be replaced by a neutral potassium (K) salt. Consequently, 2M KCl has become the accepted extractant for laboratory analysis of soil mineral nitrogen (SMN) whether it be NO_3-N, NH_4-N, or both (Griffin et al., 1995; Maynard et al., 2007; Mulvaney, 1996).

Soil NO_3-N extracted following the SNQT methodology recommends using 0.01M $CaCl_2$ as the extracting solution. In the field setting where parsimony is valued, NO_3-N is used as the proxy for SMN. Nitrate strip test technology indicates K^+ in concentrations greater than 1000 mg L^{-1} influence test results through interference (Reflectoquant Nitrate Test, Cat. No. 1.16995.001, EMD Millipore Corporation, Billerica, MA), thus, using 2M KCl as an extractant is not suitable. The alternative 0.01M $CaCl_2$ has been recommended over simpler extracts such as water because of

its flocculating effects on soil suspensions (Schmidhalter, 2005). Bringing soil particles out of suspension to create a clear supernatant is necessary for the use of the test strip technology. Consequently, 0.01M $CaCl_2$ is the recommended extractant for the SNQT methodology especially when used on soil with high clay content.

Development of empirical soil moisture correction factors

The objective of the SNQT is to obtain a measurement of NO_3-N that can be taken in the field and quickly used to make N fertilizer decisions without the need of additional laboratory measurements. Because the SNQT measures NO_3-N from a moist soil sample, converting results to a dry soil is required for correct interpretation. The SNQT read out from the nitrate test strip and reflectometer provides a concentration of nitrate (NO_3^-) ions per volume of the extraction solution. Correcting nitrate test strip values to a dry soil equivalent requires knowing the volume of extracting solution, the oven dried equivalent mass of the soil sample, the volume of water contained in the soil sample, and the mole fraction of nitrogen in a molecule of a nitrate. Measuring the oven dry equivalent mass of the soil sample and the volume of water contained in the soil sample requires the use of precision balances and drying ovens. Although these measurements are simple, they are nearly impossible to do in the field and require a minimum 24 hours to complete. The additional process of soil moisture determination further delays the availability of the SNQT results.

To simplify the correction process of the SNQT results to a dry soil equivalent, we derived empirical correction factors for our specific soil types following methods reported by Hartz (1994). Empirical correction factors are used to quickly correct nitrate strip test results taken in the field by qualitative estimations of soil moisture. To derive our correction factors we used 73 soil samples from our accuracy assessment experiment. We divided our samples into groups by gravimetric moisture contents in the range of 15-25%, 25-35%, and ≥ 36% and categorized them as dry, wet, and very wet, respectively. For each soil sample we measured the mass associated with the volumetric measurement of 10 mL of field moist soil and calculated water content. For each of our moisture groups we calculated the mean oven dry equivalent soil weights and the mean water weight associated with 10 mL from all the samples within the group. Finally using our

calculated means, we derived our empirical correction factors for each moisture group (Table 2.2) through the equation:

$$CF = \frac{1}{(V_e \div M_s \times X_i)} \quad \text{[EQN 2.2]}$$

Where, CF is the correction factor, V_e is the volume of extractant (30 mL of 0.01 *M* $CaCl_2$) + soil water from sample, M_s is the oven dry equivalent (Schroder et al.) mass of soil, and X_i is the mole fraction of N in a molecule of nitrate. As an example, in 10mL of field moist soil with a gravimetric moisture content of 20%, if we determine that ODE = 16.5g and soil water = 3mL, using EQN.2.2. we would calculate a correction factor of 2.2.

Table 2.1. Location, management type and soil taxonomic information of important agricultural soils used for accuracy assessment of the SNQT method

Island	Farm (Site)	N mgt. Practice	Soil Series	Soil Classification	Textural Class
Oahu	Helemano	Conventional	Wahiawa	Very-fine, kaolinitic, isohyperthermic Rhodic Haplustox	Silty clay
Oahu	Wahiawa	Organic	Wahiawa	Very-fine, kaolinitic, isohyperthermic Rhodic Haplustox	Silty clay
Oahu	Wahiawa	Hybrid	Wahiawa	Very-fine, kaolinitic, isohyperthermic Rhodic Haplustox	Silty clay
Oahu	Waimanalo	Conventional	Waialua	Very-fine, mixed, superactive, isohyperthermic Pachic Haplustolls	Silty clay
Oahu	Waimanalo	Organic	Waialua	Very-fine, mixed, superactive, isohyperthermic Pachic Haplustolls	Silty clay
Oahu	Waimanalo	Native	Waialua	Very-fine, mixed, superactive, isohyperthermic Pachic Haplustolls	Silty clay
Maui	Makawao	Hybrid	Keahua	Fine, kaolinitic, isohyperthermic Ustic Haplocambids	Silty clay
Maui	Makawao	Native	Keahua	Fine, kaolinitic, isohyperthermic Ustic Haplocambids	Silty clay
Maui	Kula	Conventional	Keahua	Fine, kaolinitic, isohyperthermic Ustic Haplocambids	Silty clay
Maui	Kula	Organic	Kamaole	Clayey fragmental, mixed, semiactive, isothermic Aridic Haplustolls	Stony silty loam
Hawaii	Kamuela	Conventional	Waimea	Medial, amorphic, isothermic Humic Haplustands	Very fine sandy loam
Hawaii	Lalamilo	Organic	Waimea	Medial, amorphic, isothermic Humic Haplustands	Very fine sandy loam
Hawaii	Kamuela	Native	Waimea	Medial, amorphic, isothermic Humic Haplustands	Very fine sandy loam
Hawaii	Kamuela	Conventional	Maile	Hydrous, ferrihydritic, isothermic Acrudoxic Hydrudands	Silt loam
Hawaii	Kamuela	Native	Maile	Hydrous, ferrihydritic, isothermic Acrudoxic Hydrudands	Silt loam
Hawaii	Kamuela	Organic	Paauhau	Medial hydrous, amorphic, isohyperthermic Dystric Haplustands	Silty clay loam
Oahu	Wainae	Conventional	Lualualei	Fine, smectitic, isohyperthermic Typic Gypsitorrerts	Clay
Oahu	Waianae	Organic	Lualualei	Fine, smectitic, isohyperthermic Typic Gypsitorrerts	Clay
Oahu	Waianae	Native	Lualualei	Fine, smectitic, isohyperthermic Typic Gypsitorrerts	Clay

Identification of the SNQT critical concentration

The SNQT critical concentration denotes the soil NO_3-N concentration separating expected crop fertilizer N responsive and unresponsive soils where crop response to added N is expected when soil NO_3-N concentration is below the critical concentration and not expected when soil NO_3-N concentration is above the critical concentration. To determine the SNQT critical concentration for napa cabbage (*Brassica rapa subsp. pekinensis var.Yuki F1 hybrid*), we conducted a N fertilizer rate experiment in the summer of 2017 at the University of Hawaii's Poamoho Agricultural Research Station on the island of Oahu. The Poamoho Agricultural Research Station is located in Central Oahu and is characterized by a humid tropical climate. Total annual rainfall in the Central Oahu area ranges from 1016 to 1524 mm with mean monthly rainfall of 147 mm in January and 51 mm in July (Giambelluca, et al., 2013). Mean annual daytime temperature in Central Oahu is 22°C with a mean monthly temperature of 20.5°C in January and 24°C in July (Soil Survey Staff 2016). Soil at the site is a Wahiawa series (very-fine, kaolinitic, isohyperthermic Rhodic Haplustox) (USDA 2016a).

Experimental setup/procedure

In order to establish a range of soil N concentrations from deficient to excessive, five seasonal N fertilizer treatments of 0, 50, 100, 150, and 200 kg N ha^{-1} were applied to each of two blocks (low SMN and high SMN). The treatments were replicated four times making a total of 40 experimental plots arranged in a randomized split block. The high residual SMN block was amended with a per-plant application of urea (46-0-0) fertilizer at a rate of 50 kg N ha^{-1}. The low residual SMN block, received no pre-plant urea N fertilizer. To create the blocks, we conducted 40 initial soil nitrate tests to a soil depth of 30 cm. From the initial soil nitrate tests it was determined that the soil NO_3-N concentration within the entire experimental area was ≤ 6 mg kg^{-1}. We then randomly assigned half of the experimental area as the high residual SMN block and the other half as the low SMN block. Each of the 5 N fertilizer treatments were applied in four split-applications at day 7, 21, 28, and 35 after transplanting as urea through the local irrigation system.

We designed the plots to replicate the typical local commercial farmer's planting configurations. Each plot was 1.5 m wide by 6 m long and consisted of mounded beds separated by 0.6 m wide furrows between plots. Within each plot, four rows of napa cabbage were planted with a row spacing of 0.375 m and a within-row spacing of 0.356 m. The first and last 0.38 m of mounded bed space of each plot was left unplanted. The total number of plants per plot was 60 plants consisting of 4 rows with 15 plants per row and planting density of 53,820 plants ha^{-1}.

Irrigation was supplied throughout the experiment by the use of drip tape with two lines per mounded bed, each line creating a sufficient wetting front to provide water for two plant rows. Prior to planting, potassium (K) and phosphorus (P) fertilizers were applied and tilled into the soil at rates of 120 kg ha^{-1} of K as muriate of potash (MOP) and 109 kg ha^{-1} of P as triple superphosphate (TSP). No soil liming materials were applied. Preliminary soil pH measurements (n=40) (conducted in a 1:1 soil:water suspension) showed that the soil pH within the entire experimental area was between 6.21 and 7.89. Potassium fertilizer was re-applied twice at a rate of 60 kg ha^{-1} as MOP at weeks 4 and 5 through irrigation lines. No other fertilizers or micronutrients were applied during the experiment.

One insecticide application of Emamectin benzoate marketed under the trade name Proclaim (Syngenta Crop Protection, Inc., Greensboro, North Carolina) was applied at week five to control lepidopteran pests. Weeds were controlled solely through manual hand removal. Seeding of the napa cabbage was done three weeks in advance of transplanting into the experimental plots. Napa cabbage F1 hybrid seeds of the Yuki variety treated with Thiram (Sakata Seed America, Morgan Hill, CA.) were seeded into Pro-mix biofungicide growing medium (Premier Tech Horticulture, Quakertown, PA.) using 128 cell starter trays on May 3rd 2017. During the seedling developmental stage, soluble liquid fertilizer 20-20-20 was applied at day 7 and 14 in a dilute solution. While in starter trays, one application of Cyantraniliprole under the trade name Verimark (DuPont Crop Protection, Wilmington, DE.) was applied at day 20 for control of lepidopteran pests. The seedlings were transplanted into the experimental plots 21 days after sowing. In total, 2,400 seedlings were divided among forty plots and transplanted by hand.

Data collection/analysis

The main objective of the experiment was to determine a critical NO_3-N concentration for napa cabbage by plotting measured crop yield at levels of soil NO_3-N measured at critical time points throughout the crop cycle. To do so, we measured soil NO_3-N concentrations in the active root zone (0-30 cm) as well as the subsoil (30-60cm) utilizing the SNQT procedure described above. SNQT measurements were taken at a weekly interval throughout the crop cycle. During weeks in which fertilizer treatments were applied, soil sampling was done immediately before applying N fertilizer treatments.

We collected yield measurements from each treatment at harvest. Harvest, which we conducted 49 days after transplanting and 70 days from seeding, was kept the same for all treatment plots in this experiment. Yield measurements included total above ground biomass, marketable biomass and whole plant N content. To measure yield parameters we randomly selected and harvested 8 representative whole plants per plot and weighed them in the field for total above ground biomass. Of the 8 representative plants, 4 were selected at random, separated into marketable biomass and residue biomass, and each component measured for weight.

Statistical analysis used for accuracy assessment of the SNQT

Following procedures outlined in Hartz, 1994, a linear regression analysis was conducted using SigmaPlot (Systat Software, Inc., San Jose,CA). The relationship between soil NO_3-N concentration measured by the SNQT procedure (determined on a fresh weight basis and adjusted to a dry soil basis using the actual gravimetric moisture content) and the standard laboratory method was quantified by the linear regression analysis. We regressed SNQT values on the standard laboratory method values and regression coefficients as well as the coefficient of determination were determined (EQN 2.3):

$$f = y_0 + ax \qquad \text{[EQN 2.3.]}$$

Where, f = predicted SNQT value, a = the (slope) of the line, y_0 = y-intercept, and x = laboratory method value.

To quantify differences between the two soil testing methods the mean error (ME) between the actual values from the two methods was calculated in Excel (Microsoft Excel 2010) using the equation:

$$ME = average\ (\sum_{i=1}^{n}(SNQT_i - Standard\ method_i)) \quad \text{[EQN 2.4.]}$$

Where, ME = mean error, $SNQT_i$ = SNQT values, and $Standard\ method_i$= standard laboratory method values, and n is the total number of samples.

To simplify the correction of the SNQT results to dry soil equivalence without the need for gravimetric moisture content measurement, we developed empirical correction factors for three moisture categories (Table 2.2). After we corrected our results to a dry soil equivalence using our correction factors we reassessed its accuracy.

Table 2.2. Empirically derived moisture correction factors used to correct SNQT results to a dry soil equivalence

Soil Moisture	Correction Factor
Dry	2.2
Wet	2.0
Very wet	1.7

After correcting the SNQT results using the correction factors, reassessment with a linear regression analysis was conducted to assess the relationship of soil NO_3-N concentration measured by the SNQT procedure and the standard laboratory method. Following regression analysis in which SNQT values were regressed upon the standard laboratory method values, a similar set of statistics including regression coefficients and the coefficient of determination were determined using the linear equation (see EQN 2.3). Similarly the mean error (ME) between the actual values from the two methods was calculated in Microsoft Excel using equation (EQN 2.4)

When the SNQT is used as a pre-sidedress soil nitrate test, the responsive range of most importance to the decision making process falls between 0-40 mg kg^{-1}(Hartz, 1994). It is within this range that the SNQT must be most accurate in order to have value as an in season diagnostic tool. To assess the performance of the SNQT within this range, we excluded all the samples with soil NO_3-N concentrations over 40 mg kg^{-1} from our data set and conducted an

additional linear regression analysis in Sigma Plot (Systat Software, Inc., San Jose,CA). We used the same regression approach outlined above.

Many previous studies have determined a soil NO_3-N critical concentration that indicates a threshold in which no yield response to N fertilizer is expected. In such studies the soil NO_3-N was determined using the standard laboratory method. If we intend to use the SNQT as a substitute for the standard laboratory method, we need to know how well the SNQT predicts results for the standard laboratory method. To assess how well the SNQT can predict the standard laboratory method values, we conducted a linear regression in which the standard laboratory method was regressed upon the SNQT. New sets of statistics including regression coefficients, coefficients of determination, and a 95% prediction band were determined using the linear equation (see EQN 2.3).

Statistical analysis for the development of SNQT critical concentrations

We developed SNQT critical levels for napa cabbage grown on a Rhodic Haplustox by quantifying the relationship between soil NO_3-N and relative yield using four different statistical models. We expected to identify which model was most useful in relating soil test data to crop yields. Relative yield data was plotted as a function of measured soil NO_3-N data at weekly intervals throughout the cropping period. The models that were compared include: 1) Cate-Nelson analysis (Cate and Nelson, 1971), 2) Linear-response plateau (see EQN 2.5), 3) a 2-parameter Mitscherlich equation (see EQN 2.6), and 4) a 3-parameter Mitscherlich equation (see EQN 2.7).

The Cate-Nelson approach is semi-quantitative in that it relates relative yields to soil NO_3-N values by plotting relative yields as a function of soil NO_3-N and then visually dividing data into N–responsive and nonresponsive categories. N-responsive and nonresponsive sites are identified by superimposing horizontal and vertical lines on the scatter plot to make four quadrants, with the objective of minimizing points in the upper left and lower right hand quadrants. The point at which the vertical line intersects the x-axis is termed the “critical concentration” and is used to split the data into N-responsive and non-responsive categories. The

horizontal line is arbitrarily set to an acceptable value of relative yield. Data points that fall in the upper right quadrant or bottom left quadrant have yield responses in agreement with the SNQT critical concentration. Whereas, data points in the upper left and bottom right quadrants contradict the SNQT critical concentration. For example, points that reside in the upper left quadrant are recommending N fertilizer in non-responsive sites (over prediction), and points that reside in the bottom right quadrant are recommending no N fertilizer in cases where response is expected resulting in yield reductions (under prediction). Once quadrants are developed, percentages of data points in the respective quadrants for N fertilizer over predictions, under predictions, and correct predictions can be calculated. We calculated the percentage of experimental points in each quadrant by taking the quotient of points in a specific quadrant over the total number of points in the graph.

Because the Cate Nelson's procedure is a semi-quantitative approach, we also used three alternative mathematical models (mentioned above) as quantitative approaches for comparison. Through model fitting we used parameterization data to identify a SNQT critical concentration based upon the different models. We used best fit statistics to identify which model provided the best fit SNQT critical concentration. Best fit statistics used included: regression coefficients, coefficients of determination, ME, MSE, RMSE, PRESS statistics and levels of significance were determined using the Sigmaplot software (Systat Software, Inc., San Jose,CA).

The linear-response plateau equation is the following:

$$f = a + b * (if(x \leq node, x, node)) \qquad \text{[EQN 2.5.]}$$

Where f = the fitted line based on predicted values from the equation, a = the y-intercept or the expected marketable biomass with a soil NO_3-N concentration of zero, b = the slope or relationship between yields and biomass as a linear function up until the response plateau, x = the explanatory variable or the measured soil test values, $node$ = the junction between the linear and non-responsive parts of the model corresponding to the nitrate critical concentration.

The 2-parameter Mitscherlich equation is the following:

$$f = a(1 - \exp(^{-bx})) \quad \text{[EQN 2.6.]}$$

Where f = the fitted line based on predicted values from the equation, a = the asymptote or the biological maximum attainable yield, b = the rate of change or the change in yield to each incremental change in soil nitrate concentration, x = the explanatory variable or the measured soil test values.

Lastly, the 3-parameter Mitscherlich equation is the following:

$$f = y_0 + a(1 - \exp(^{-bx})) \quad \text{[EQN 2.7.]}$$

Where f = the fitted line based on predicted values from the equation, a = the asymptote or the biological maximum attainable yield, b = the rate of change or the change in yield to each incremental change in soil nitrate concentration, x = the explanatory variable or the measured soil test values and , y_0 = the y-intercept or the expected marketable biomass with a soil NO_3-N concentration of zero. Note that the 3-parameter Mitscherlich equation estimates a y-intercept, which is a value for yield at zero levels of soil nitrate.

Results

Accuracy assessment of the SNQT

We observed that the SNQT provided an acceptable measure of soil NO_3-N concentrations. The SNQT had a slight over-prediction throughout the range of soil types and soil NO_3-N concentrations tested in this study. The range of NO_3-N concentrations in the soil samples used for this calibration was 2.86 to 276 mg kg^{-1} with a trend of increasing over-prediction to increasing soil NO_3-N.

Linear regression analysis revealed that the SNQT was closely related with the standard laboratory method of analysis, with an adjusted $r^2 = 0.96$ (DF= 72, and $p<0.0001$) (Figure 2.1). The SNQT values, for this comparison, where converted to a dry soil basis using the actual moisture content of the field moist samples rather than by using a correction factor. We note that the SNQT method slightly over-predicted laboratory soil NO_3-N by roughly 6 mg N kg^{-1}. Over-estimation from the SNQT occurred over the entire range of soil NO_3-N concentrations. The

degree of over estimation at the low soil NO_3-N concentrations is depicted by the y-intercept (y_0 = 6.09) and the change in error as soil NO_3-N increased is depicted by the slope (a= 1.02) (Figure 2.1.). The ME (mean error) between the SNQT values and the standard laboratory values was 8.27 which also indicates that the SNQT slightly over predicts soil NO_3-N concentrations with an average value of 8.27 mg kg^{-1}.

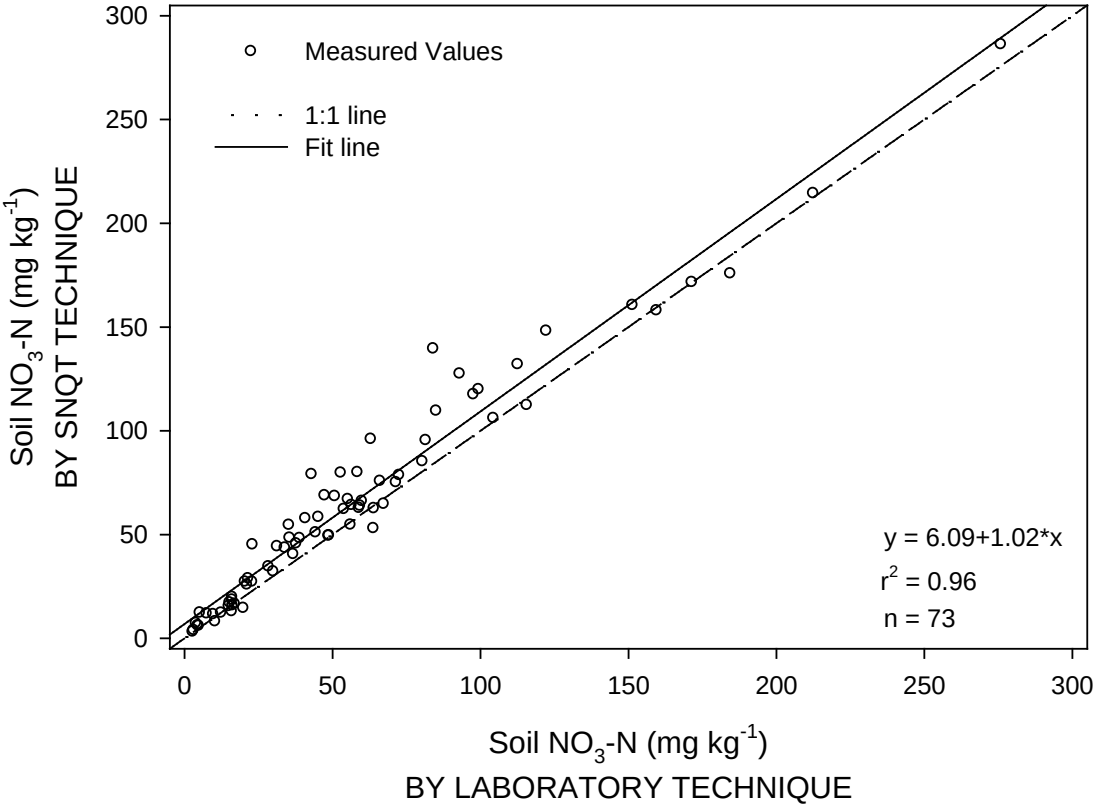


Figure2. 1. *Accuracy assessment of the soil NO_3-N quick test method (SNQT) compared to the standard laboratory method of soil NO_3-N determination conducted on a wide range soil types important to Hawaii's agricultural landscape. Field moist soil NO_3-N values were adjusted using the laboratory measured moisture content to report NO_3-N concentration a dry soil basis. Regression analysis showed generally good agreement with only a slight over-prediction of the standard laboratory method across a large range of soil NO_3-N concentrations.*

Development of empirical correction factors

The SNQT was an effective method of obtaining rapid, field estimates of soil NO_3-N. It is thus an improvement over standard laboratory methods considering that the SNQT measures NO_3-N at a point in time close to the moment in which N fertilizer decisions are best made. However, results from the nitrate strip test on field moist soil need to be corrected to a dry soil basis. Correction of soil NO_3-N estimations to a dry soil basis is not possible in the field without a correction factor.

Similar to the approach described by Hartz, (1994), we derived correction factors of 2.2, 2.0, and 1.7 for dry, wet, and very wet soils, respectively (Table 2.2) using equation 2.2. For all the soil samples, measured field-moist water content varied from 15% to 116%. Based on a volumetric addition of 10 mL of field-moist soil, the dry, wet, and very wet groups contained mean oven dry weights of 16.65, 15.71, and 14.02 g soil, and mean gravimetric moisture contents of 20%, 27%, and 43%, respectively. The empirical correction factors were used to quickly convert field-measured test strip values to values based on volume, which are read as NO_3 mg L^{-1}, and converted to NO_3-N mg kg^{-1} based on dry soil as described in equation 2.8 using the correction factors in Table 2.2:

$$SNQT\ reading\ (NO_3^- mg\ L^{-1}) \div correction\ factor = \ NO_3 - N\ mg\ kg^{-1} \qquad \text{[EQN 2.8.]}$$

When SNQT NO_3-N concentrations were converted using the empirically derived correction factors, repeating the linear regression analysis revealed that the field-moist SNQT measurements remained closely related to the standard laboratory method values with an adjusted $r^2 = 0.95$ (DF=73, and $p<0.0001$) (Figure 2.2). This result confirms that using the correction factors to convert NO_3-N estimates to a dry soil basis is acceptable and does not significantly affect the accuracy of the test. The ME between our corrected SNQT values and the standard laboratory method values was 10.26 confirming that the SNQT methodology over predicts laboratory soil NO_3-N concentrations even when including correction factors.

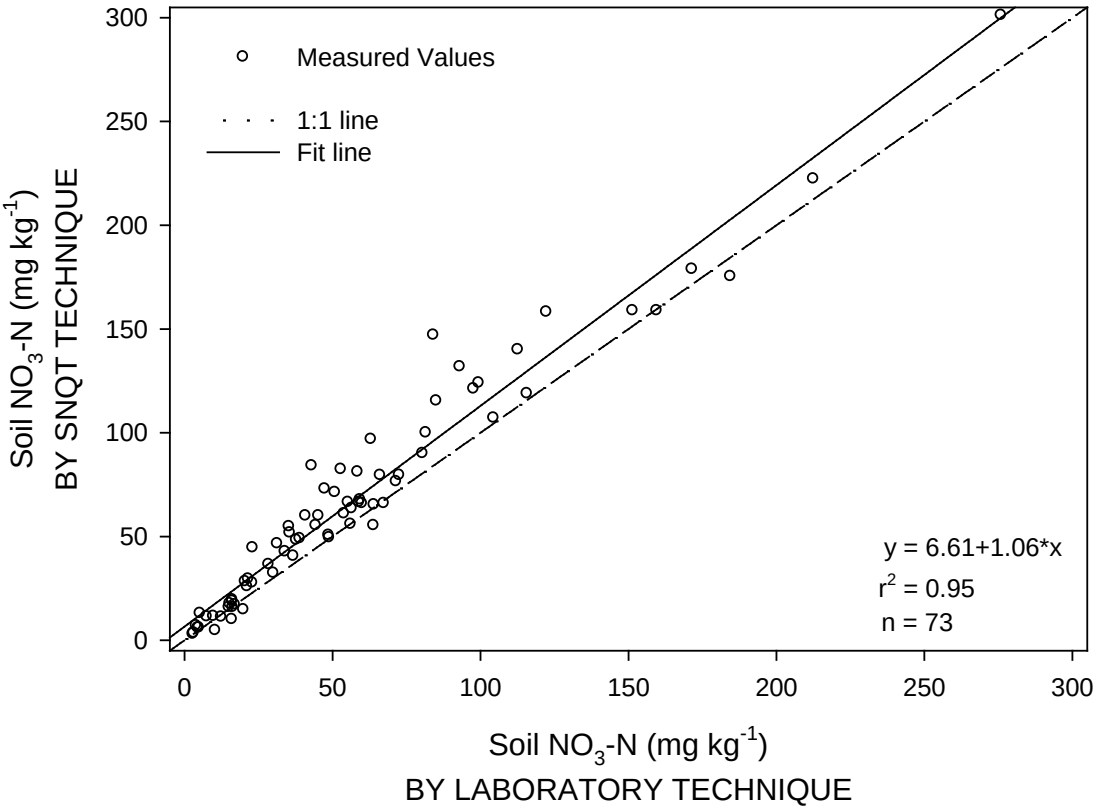


Figure2. 2. *Accuracy assessment of the soil NO_3-N quick test method (SNQT) compared to the standard laboratory method of soil NO_3-N determination conducted on a wide range soil types important to Hawaii's agricultural landscape. Field moist soil NO_3-N (SNQT) values were adjusted using an empirical correction factor to report NO_3-N concentration a dry soil basis. Regression analysis again revealed a close agreement with the standard laboratory method when our correction factor was used to convert nitrate test strip values to NO_3-N concentration a dry soil basis.*

Accuracy assessment of SNQT in the responsive range

When only samples within the responsive range of 0-40 mg kg^{-1} range were used, linear regression analysis revealed that SNQT values in this important diagnostic range retained a high degree of agreement to the standard laboratory method. However, with this subset of data the coefficient of determination decreased from an adjusted $r^2 = 0.95$ (full set) to an adjusted $r^2 = 0.84$, DF= 24, and $p<0.001$(Figure 2.3). We again found that for values in the range of 0-40 mg kg^{-1} the SNQT method slightly over estimated laboratory soil NO_3-N. The degree of over estimation is depicted by the y-intercept of the fitted line ($y_0 = 0.23$), which is greater than zero and slope of 1.12, which is greater than a slope of 1.0. The mean error calculated between the SNQT and the standard laboratory method in this critical range of values was 1.88 mg kg^{-1}, which confirms that the SNQT method offers a higher degree of accuracy in this critical range than the accuracy within the full range of soil NO_3-N concentrations.

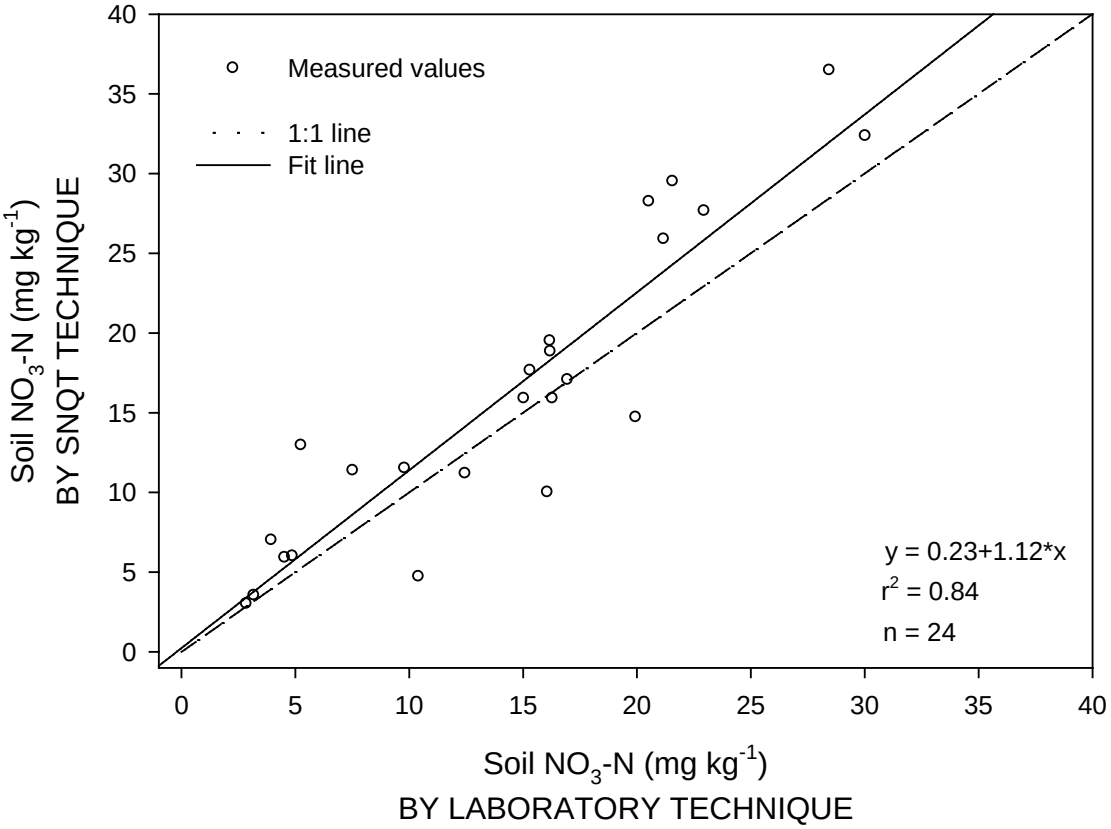


Figure2. 3. *Accuracy assessment of the soil NO_3-N quick test (SNQT) method compared to the standard laboratory method of soil NO_3-N determination conducted on only samples within the critical range of 0-40 mg kg^{-1} NO_3-N. Field moist soil NO_3-N values were corrected using an empirical correction factor to report NO_3-N concentration a dry soil basis. The fitted regression equation was still in close agreement with the standard laboratory method.*

SNQT prediction of Standard laboratory method

When we ran another regression analysis on the entire range of soil NO_3-N concentrations by regressing the standard laboratory method values on the SNQT values to assess how well the SNQT methodology can predict laboratory measurement of soil NO_3-N (Figure 2.4). When considering the entire range of soil NO_3-N concentrations in this study, we found that the two test methods were in excellent agreement with an $r^2 = 0.95$. For visual determination of the prediction, we plotted the 1:1 line and then plotted 95% prediction bands from our linear regression (Figure 2.4). As an alternative method of assessing the SNQT prediction accuracy of the standard laboratory method we also calculated the mean square error between the SNQT method and the standard laboratory method nitrate values. We found that the mean square error between the values from the two tests was 10.26 mg kg^{-1}, which indicates that across our sample population the SNQT over predicts the values derived from the standard laboratory method by 10.26 mg kg^{-1} NO_3-N. A quick analysis of figure 2.4 also indicated that the departure from a 1:1 line is largest as values greater than 50 mg kg^{-1} NO_3-N, which are above the range in which fertilizer application amounts are predicted (largely 0-40 mg kg^{-1} NO_3-N).

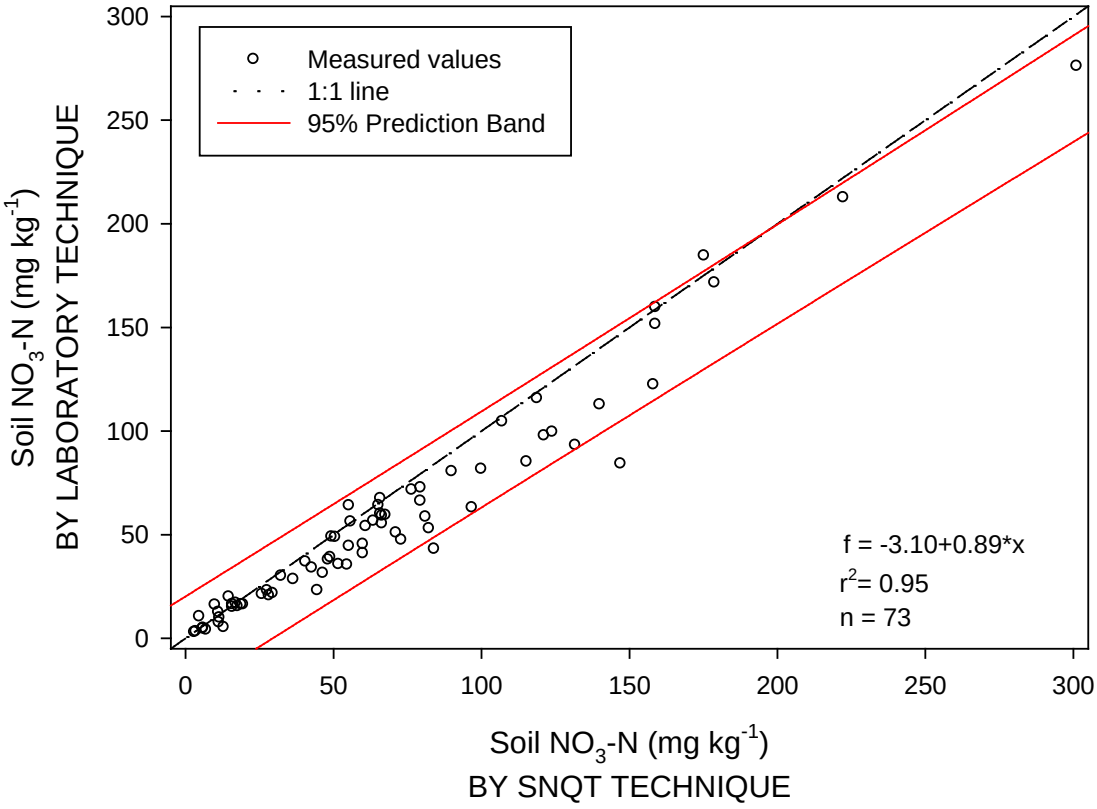


Figure2. 4. *Soil NO_3-N quick test method (SNQT) prediction bands when the soil NO_3-N quick test is used to predict values from the standard laboratory method of soil NO_3-N determination. The quick test method adjusted field moist soil NO_3-N values to a dry soil basis using our correction factor.*

SNQT Critical Concentration

The SNQT critical concentration is a threshold value that indicates whether N fertilizer should be applied or not. Using data from our N fertilizer rate experiment as a basis to create general guidelines for use of the SNQT as a pre-sidedress soil nitrate test, we set out to determine critical NO_3-N concentrations that identify crop responsiveness to additional N fertilizer as well as optimal timing for use. Soil nitrate concentrations observed throughout the fertilizer rate experiment ranged from 0 to 310 mg kg^{-1}.

Modelling results indicated that the optimal timing for use of the SNQT as a diagnostic indicator of yields was determined to be 2 weeks and 3 weeks after planting (see table 2.3.). Based on the coefficients of determination from our model fitting procedures weeks 2 followed by 3 had the closest fits which were unanimous amongst all models used. When soil NO_3-N was measured 2 weeks after planting, the linear-response plateau fit with an adjusted r^2= 0.4221, the 2-parameter Mitscherlich fit with an adjusted r^2 = 0.4458, and the 3-parameter Mitscherlich fit with an adjusted r^2 = 0.4309. When soil NO_3-N was measured 3 weeks after planting, the linear-response plateau fit with an adjusted r^2= 0.3866, the 2-parameter Mitscherlich fit with an adjusted r^2 = 0.4127, and the 3-parameter Mitscherlich fit with an adjusted r^2 = 0.4024.

Table 2.3. Best fit statistics used to determine the optimum timing for use of the SNQT in relation to napa cabbage yield.

Weeks after planting	Adjusted r^2 values from model fitting procedure		
	Linear-response plateau	2-parameter Mitscherlich	3-parameter Mitscherlich
0	0.2955	0.2305	0.1027
1	0.1824	0.108	0.138
2	0.4221	0.4458	0.4309
3	0.3866	0.4127	0.4024
4	0.3405	0	0.3752

Adjusted coefficients of determination (adjusted r^2 values) were used to compare model fits of relative yields plotted as a function of soil NO_3-N values measured in the field setting. Comparisons were among three mathematical models between 0-4 weeks after planting.

Using the Cate-Nelson approach (Cate and Nelson, 1971), we determined critical NO_3-N concentrations of 38 and 37 mg kg^{-1} for weeks two and three, respectively (Figure 2.5.). When used 2 weeks after planting, the quadrants derived from the Cate-Nelson procedure predicted the need for N fertilizer correctly (points in lower left + upper right quadrants) 75% of the time (30 out of 40 comparisons), while it recommended the need for fertilizer in non-responsive sites (upper left quadrant) 5% of the time (2 out of 40 comparison), and recommended no fertilizer needed where response was expected (lower right quadrant) 20% of the time (8 out of 40 comparisons). When used 3 weeks after planting, the Cate-Nelson procedure predicted the need for N fertilizer correctly (points in lower left + upper right quadrants) 75% of the time (30 out of 40 comparisons), while it recommended the need for fertilizer in nonresponsive sites (upper left quadrant) 7.5% of the time (3 out of 40 comparisons), and recommended no fertilizer needed in plot which yields were reduced (lower right quadrant) 17.5% of the time (7 out of 40 comparisons).

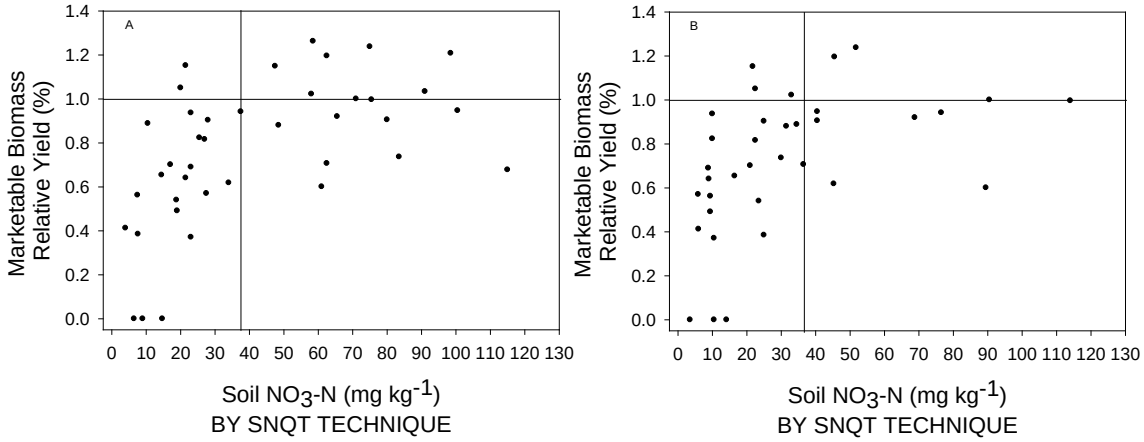


Figure 2.5 SNQT critical concentrations identified by the Cate Nelson analysis. Soil NO_3-N concentration in the surface 30 cm of soil were measured using the SNQT methodology and interpreted to a dry soil bases using empirical correction factors. A) SNQT measurement taken 2 weeks after planting; B) SNQT measurements taken 3 weeks after planting.

The linear response plateau model predicted 95% of relative yield would occur at critical NO_3-N concentrations of 32.18 and 34.07 mg kg^{-1}, for weeks 2 and 3, respectively (Figure 2.6). The 2-parameter Mitscherlich predicted maximum 95% of relative yield would occur at higher critical NO_3-N concentrations of 57.77 and 49.65 mg kg^{-1} for the same time increments respectively (Figure 2.7.). The 3-parameter Mitscherlich model predicted maximum 95% of relative yield would occur at the NO_3-N concentrations of 57.85 and 51.00 mg kg^{-1}, respectively (Figure 2.8.). The 3-parameter Mitscherlich model thus predicted 95% of relative yield would occur at the highest levels of NO_3-N, when comparing the three models. SNQT critical concentrations varied significantly depending on which model was used while best-fit statistics (RMSE and PRESS) were almost identical for all models for both weeks 2 and 3 (Tables. 2.4 and 2.5). Thus, choice of model based on best-fit statistics alone is difficult.

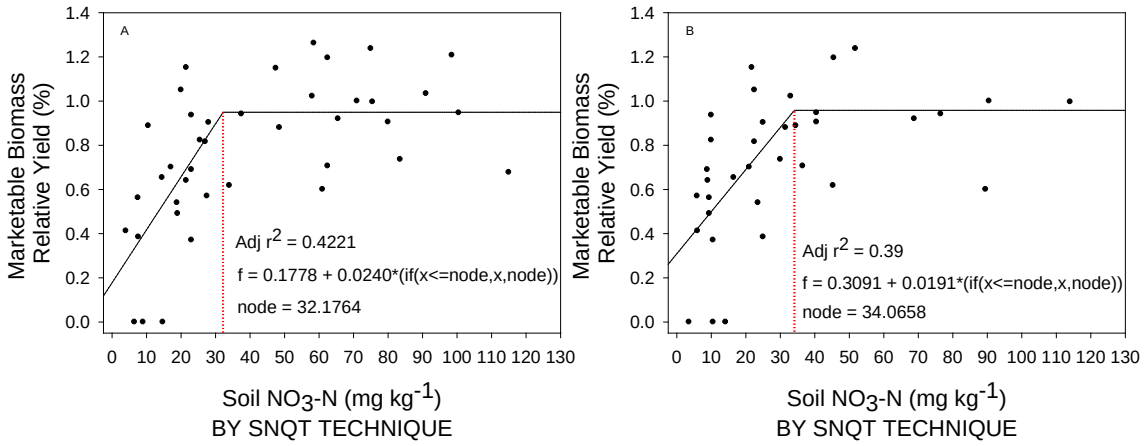


Figure 2.6. SNQT critical concentrations identified by the linear-response plateau model. Soil NO_3-N concentration in the surface 30 cm of soil were measured using the SNQT methodology and corrected to a dry soil basis using empirical correction factors previously determined. A) Measurements taken 2 weeks after planting; B) Measurements taken 3 weeks after planting. (f= relative yields; x = soil NO_3-N)

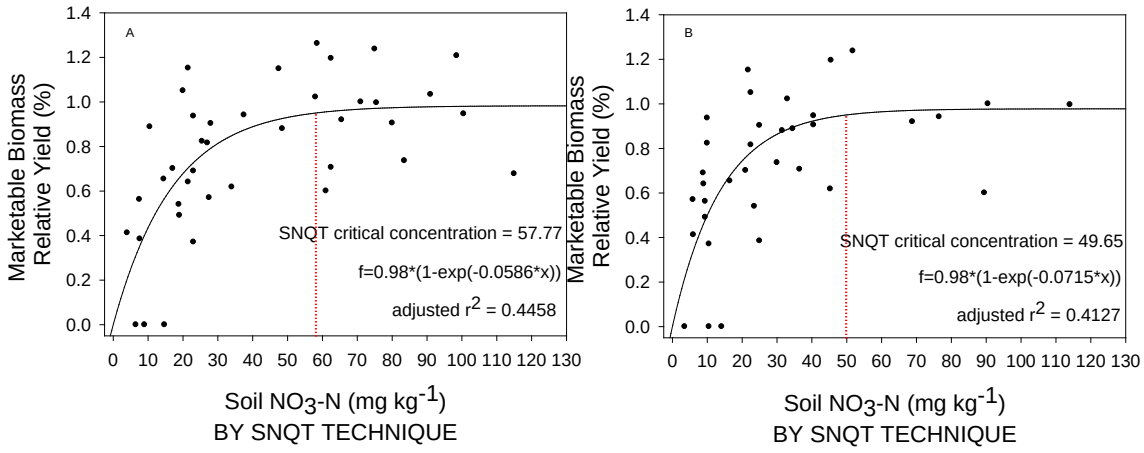


Figure 2.7 SNQT critical concentrations identified by the 2-parameter Mitscherlich model as required for 95% of relative yield. Soil NO_3-N concentration in the surface 30 cm of soil were measured using the SNQT methodology and corrected on a dry soil basis using empirical correction factors previously determined. A) Measurements taken 2 weeks after planting; B) Measurements taken 3 weeks after planting. (f= relative yields; x = soil NO_3-N)

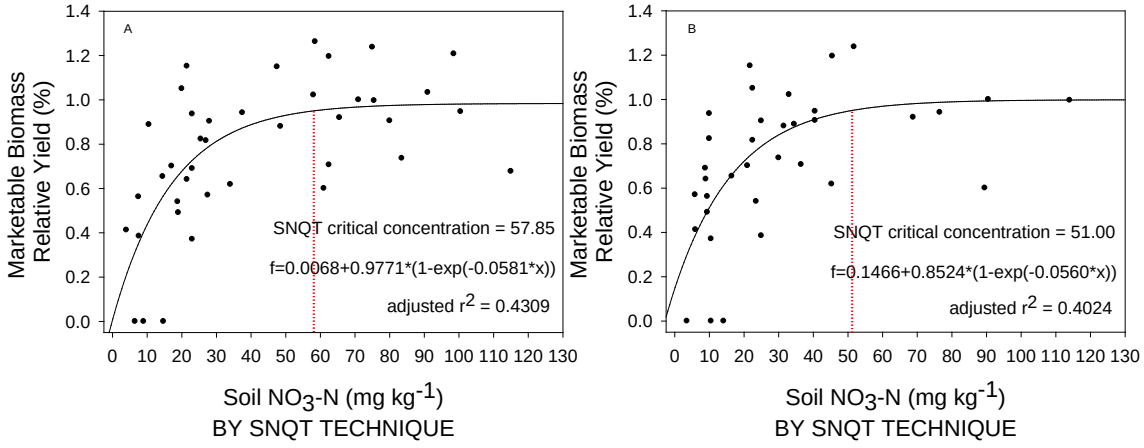


Figure 2.8 SNQT critical concentrations identified by the 3-parameter Mitscherlich model as required to obtain 95% of relative yield. Soil NO_3-N concentration in the surface 30 cm of soil were measured using the SNQT methodology and corrected to a dry soil basis using empirical correction factors previously determined. A) Measurement taken 2 weeks after planting; B) Measurements taken 3 weeks after planting. (f= relative yields; x = soil NO_3-N)

Table 2.4. Statistical models used to determine critical concentration of soil NO3-N two weeks after planting

Model	Equation	adj R^2	RMSE	MSE	PRESS	P-value	Node	p-value(node)
LP§	Y = 0.1778 + 0.0240 X	0.4221	0.2386	0.0569	2.6632	<0.0001	32.1764	<0.0001
MIT-2	Y = 0.9833 × (1 - exp(-0.0586 × X))	0.4458	0.2367	0.0560	2.4875	<0.0001		
MIT-3	Y = 0.0068 + 0.9771 × (1 - exp(-0.0581 × X))	0.4309	0.2367	0.0560	2.6556	<0.0001		

LP = Linear-response plateau, MIT-2 = Mitscherlich(2 parameter), Mit-3 = Mitscherlich(3 parameter)
X = soil NO_3-N values, §= *Equation shown applies for X values less then Node value*

Table 2.5. Statistical models used to determine critical concentration of soil NO3-N three weeks after planting

Model	Equation	adj R^2	RMSE	MSE	PRESS	P-value	Node	p-value (node)
LP§	Y = 0.3091 + 0.0191 X	0.3866	0.2458	0.0604	2.7876	<0.0001	34.0658	<0.0001
MIT-2	Y = 0.9781 × (1 - exp(-0.0715 × X))	0.4127	0.2437	0.0594	2.6475	<0.0001		
MIT-3	Y = 0.1466 + 0.8524 × (1 - exp(-0.0560 × X))	0.4024	0.2426	0.0588	2.7604	<0.0001		

LP = Linear-response plateau, MIT-2 = Mitscherlich(2 parameter), Mit-3 = Mitscherlich(3 parameter)
X = soil NO_3-N values, §= *Equation shown applies for X values less then Node value*

Discussion

Accuracy assessment of the SNQT

The overall results from our SNQT accuracy assessment were similar to results presented in previous studies from non-tropical climates with some small differences. The coefficients of determination between the SNQT and standard laboratory methods in our study were 0.96 and 0.95 when corrected for laboratory gravimetric moisture and converted using correction factors, respectively. These results were within the range of previously reported coefficients of determination values, which ranged from 0.92 to 0.96 (Hartz, 1994; Hartz et al., 2000; Schmidhalter, 2005). The high coefficient of determination in this study suggests that the SNQT is a robust soil test for important agricultural soils of Hawaii. Contradictory to previous studies, our SNQT soil test slightly over-estimated soil NO_3-N compared with the standard laboratory methods, whereas previous studies reported under-estimates of soil NO_3-N (Hartz, 1994; Hartz et al., 2000; Hartz and Breschini, 2002; Schmidhalter, 2005). However when the range of soil NO_3-N was limited to 0-40 mg kg^{-1} the discrepancy was much lower, and thus the use of SNQT in the most important range compares better with the standard method.

Development of empirical correction factors

Following the methods described in Hartz, (1994) we derived our set of empirical correction factors to convert field-moist SNQT results to a dry soil basis required for comparison with laboratory analysis. While Hartz (1994) developed correction factors for three soil texture categories and two moisture categories, we developed correction factors for clay soils only and three moisture categories, which conforms better to Hawaii's tropical soils with soil textures characterized by high clay content (Uehara and Gillman, 1981). Moisture corrected SNQT results using our correction factors over predicted soil NO_3-N concentrations by 10.26 mg kg^{-1} when the full range of soil concentrations where used. However, the responsive range that is most important to fertilizer decision making is in the range from 0 to 40 mg kg^{-1}. In this responsive range, the average over prediction was an acceptable 1.88 mg kg^{-1}. Although the accuracy of the SNQT isn't perfect, it is an acceptable tradeoff of loss in accuracy for substantial gains in simplicity, convenience, and rapidness.

Correction factors developed in this study were derived from 56 soil samples coming from soils classified as the Wahiawa soil series and 17 samples coming from a variety of differing soil types found in Hawai‘i (Table 3.1). The empirical correction factors enable the SNQT test to be used with confidence on soils from the same or similar soil types. Different empirical correction factors are needed for the many other soil types found throughout Hawaii, especially if the soil types differ significantly in bulk density and water holding capacity such as the Andisols and Histosols.

Models to determine NO_3-N critical concentrations

Critical concentrations of SNQT NO_3-N can now be used in the field to identify scenarios where a response to added fertilizer N is to be expected for napa cabbage grown in an Oxisol. We quantified the relationship between soil NO_3-N concentrations and relative yields using four models; one semi-quantitative approach (Cate-Nelson) and three statistical approaches using mathematical models (linear response plateau, 2-parameter Mitscherlich, and 3-parameter Mitscherlich). The range of soil NO_3-N critical concentrations varied significantly depending on which model was used. We chose to use the Cate-Nelson approach, which gives the best prediction of SNQT critical concentration based on parsimony and biological significance.

The Cate-Nelson’s procedure is a commonly used approach based upon its simplicity and easily interpreted visualization of the data (Heckman et al., 1995; Heckman et al., 2002; Krusekopf et al., 2002). Although it is not a statistical method, its advantages lie in its simple visual interpretation of the data. Some may argue that it has drawbacks due to its semi-quantitative approach, which doesn’t rely on statistics when identifying a soil NO_3-N critical concentration. However, its qualitative nature means that its prediction is not as heavily influenced by outliers which can be a disadvantage of statistical based approaches.

While the three mathematical models performed similarly in their fit, the 2-parameter Mitscherlich model produced the statistically superior approach. The 2-parameter Mitscherlich is a curvilinear model fit that is forced through the y-intercept at zero and exponentially approaches a maximum value denoted by the asymptote. This model resulted in the lowest MSE, RMSE, and PRESS statistics from all models used (Table 2.4 and 2.5). The main arguments against the 2-

parameter Mitscherlich model are that yield responses to fertilizer additions often follow a threshold rather than a smooth fit. Despite the best fit using statistics, biological significance suggests the 2-parameter Mitscherlich tends to have a greater tendency to falsely identify responsive sites which means that the probability for over fertilization is greater thus increasing the potential for environmental N pollution (Anderson and Nelson, 1975). We must also take note that the statistical outputs were very similar to each other making a choice for superior model based on statistics alone difficult.

The linear response plateau is often considered the most appropriate model for these types of studies because it describes the biological plateau effect of crop response to fertilizers or increasing concentrations of a nutrient in the soil (Anderson and Nelson, 1975). The linear response plateau model is a segmented non-linear model that includes a linear increase up into a point where no response is evident signified by a node and vertical line to the x-axis, which denotes the critical concentration. The linear response plateau model is very similar in form to the Cate-Nelson simplified procedure as both lack a curvilinear component and both involve splitting soil NO_3-N data into two categories based on yield response to increasing soil NO_3-N levels . The main argument against the linear response plateau is that it tends to overestimate yields in the portion of the response curve near to the node (Anderson and Nelson, 1975). Consequently, the probability of falsely identifying unresponsive sites is larger when using the linear response plateau to predict fertilizer responsiveness, which may lead to a farmer to under-apply fertilizer with a corresponding loss in yields.

The two best performing mathematical models (2-parameter Mitscherlich and linear plateau) have the tendency to either over-estimate or under-estimate fertilizer requirement, respectively. In the former case, where the estimated critical concentration is high, over-fertilization is accompanied by unfavorable environmental consequences and undesirable economic costs to the farmer. On the other hand, the lower estimate of the critical concentration derived from the linear plateau model may penalize the farmer with lower yields. The Cate-Nelson's simplified procedure seems to be a fair compromise between the two mathematical models as it retains the ecological value of the linear response plateau, but overcomes the

weakness by allowing the manual placement of the soil test critical concentration (vertical line) to ensure optimum yields. We note that the Cate-Nelson approach and the linear plateau model produced similar critical NO_3-N concentrations for weeks 2 and 3.

Estimates of Cate Nelson's NO_3-N critical concentrations

The Cate-Nelson NO_3-N critical concentrations of 38 mg kg^{-1} measured two weeks after transplanting and 37 mg kg^{-1}measured three weeks after transplanting identified for napa cabbage in this study were high compared to the PSNT critical NO_3-N concentrations of 20 mg kg^{-1} for lettuce and celery grown in California (Hartz et al., 2000), and 24 mg kg^{-1} for head cabbage grown across New Jersey, Connecticut, Delaware, and New York (Heckman et al., 2002). Differences in estimated critical concentrations between this study and previous studies using similar vegetable crops can be attributed to higher potential N loss pathways characteristic of tropical environments as nitrate leaching and denitrification tend to be especially pronounced (Cahn et al., 1993; Ewel, 1986).

Another difference in crop growth that may cause differences in the soil NO_3-N critical concentrations is growth duration. Part of our study, which included both napa cabbage and head cabbage, reveals that major differences occur in growth duration and time at which maximum rate of NO_3-N uptake occurs (Appendix). In our growing conditions the napa cabbage growth duration was 26 days shorter than that of head cabbage. Also our data indicates that the napa cabbage maximum rate of N uptake occurred 18 days sooner from planting than for head cabbage. We also measured that, for the two weeks bracketing the maximum rate of N uptake, napa cabbage absorbed 150 kg N ha^{-1}. In contrast, the maximum rate of N uptake of head cabbage was only 110 kg N ha^{-1}, and occurred 18 days later than in napa cabbage. Thus it seems plausible that soil NO_3-N critical concentrations for a crop such as napa cabbage, with such a short crop duration and high N uptake rate during the period of logarithmic growth, must be higher than soil NO_3-N critical concentrations required for head cabbage.

Timing for use of the SNQT

The appropriate timing for use of the SNQT measurement is often determined by crop specific phenology. For example, studies on sweet corn conducted soil N tests when the plants

were 30 cm at the whorl (Heckman et al., 1995), tomatoes when plants were ≈ 10-15 cm tall (Krusekopt et al., 2002), lettuce when plants were at the two to four leaf stage (Hartz et al., 2000), and celery two weeks after transplanting (Hartz et al., 2000). Our results suggest that napa cabbage reaches a maximum N uptake rate 25 days after transplanting, and therefore, N fertilizer applications should be made before that point in time to ensure sufficient soil and fertilizer N is available to meet this need.

In our study, the most appropriate timing for use of the SNQT was two and sometimes three weeks after planting. For all three mathematical models the best fits were obtained at the two and three weeks after transplanting. These times make sense biologically because they coincide with the period directly proceeding peak N of N absorption for napa cabbage (Appendix).

Conclusion

In conclusion, the SNQT method of assessing soil nitrate in field moist soil with the use of the empirically derived correction factors is a good alternative soil test to rapidly and reliably determine in-season soil NO_3-N status across a range of mineralogically diverse Hawaiian soils. We demonstrate that the SNQT methodology can be used as a diagnostic tool to predict napa cabbage response to N fertilization in an Oxisol with a critical NO_3-N concentration of 38 mg kg^{-1}. The SNQT derived soil NO_3-N concentrations were most sensitive to the N status of the cropping system when used at two and three weeks after planting seedlings into the field. Overall assessment suggests the SNQT methodology meets many of the criteria of a good diagnostic test for N management decision support with potential to improve the economics of farming while protecting the environment.

Chapter Three

Conclusion

This study set out to adapt a diagnostic tool to rapidly measure in-field soil NO_3-N status combined with an appropriate NO_3-N critical concentration to guide N fertilizer applications in Hawaii vegetable systems. This diagnostic tool can serve as both a pre-plant soil nitrate test that indicates how much residual soil N is available to the crop at planting and a pre-sidedress soil NO_3-N test that indicates when to apply sidedress N fertilizer during the cropping season. In achieving our two objectives, we found that the soil NO_3-N quick test provided a reliable estimate of soil N status with sufficient ease and accuracy for routine in-field analysis. We also arrived at a critical NO_3-N concentration for napa cabbage grown on an Oxisol that can be used to guide the in-season timing and rate of fertilizer N application.

The research results demonstrate that the SNQT reliably measures soil NO_3-N across a wide range of concentrations (2.86 to 276 mg kg^{-1}) in a diverse set of important agricultural soils of Hawaii. The accuracy of the SNQT was greatest when soil NO_3-N was within the range of 0 to 40 mg kg^{-1}, the range where decisions regarding fertilizer application is most critical. For napa cabbage grown on a Rhodic Haplustox we identified the NO_3-N critical concentration value of 38 mg kg^{-1}. With this critical concentration value in hand, farmers and/or extension agents make fertilizer application decisions that assure acceptable crop yields while simultaneously reducing likelihood of excess N application. The SNQT, used as a pre-sidedress test during the cropping season, performed best as a diagnostic tool predicting crop yield when it was used 2-3 weeks after transplanting, which coincided with the onset of rapid crop N uptake. This tells a napa cabbage farmer that as long as soil NO_3-N concentrations at pre-plant or in-season are 38 mg kg^{-1} or greater adding fertilizer will not equate to higher crop yields. The SNQT critical concentration found in this study was higher than critical concentrations of 20 to 25 mg kg^{-1} for brassica crops

reported in the literature. However, we attribute the difference to high-yielding napa cabbage with rapid N uptake patterns grown in a tropical environment.

While the SNQT worked well across the range of soil diversity found in Hawaii, we caution the transfer of the soil NO_3-N critical concentration across the full range of soils and cropping systems. Crop growth is not only dependent on soil nutrient concentration, but is also sensitive to differences in climate, especially temperature and moisture. In Hawaii where temperature and moisture regimes vary dramatically across small spatial scales, crop growth dynamics show great variability. Nonetheless, using the SNQT and its corresponding critical concentration on the important vegetable growing areas found in Central Oahu, covering greater than 7,500 hectares (Ikawa, 1985), is reasonable because they overly the Molokai, Lahaina, and Wahiawa series, which are all Oxisols with similar mineralogy, and a comparable temperature regime (isohyperthermic). Two of the largest commercial vegetable farms are found in Central Oahu on soils classified as the Wahiawa, Lahaina, and Molokai soil series. These are intensively managed operations where ensuring high crop yields depends on sufficient N fertilizer application. Current N fertilizer applications, likely, are derived using a fertilizer response approach (person comm.), which does not account for soil N status prior to planting or during the cropping season. If large commercial vegetable farmers adopt the SNQT as a diagnostic tool, there is great potential to synchronize N fertilizer applications with crop N uptake patterns with the following potential benefits: 1) maintenance of high yields, 2) increased profitability by reducing the likelihood of excess N application, and 3) reduced potential for negative environmental impacts caused by excess N leaching into groundwater resources.

The likelihood of grower adoption of the SNQT technology depends on several conditions. First, growers must be confident that the test provides accurate and reliable results in a timely manner. Second, the test must be simple in execution and easily interpreted. Finally, the test must be cost-effective. We have shown the test to be accurate and reliable, simple and rapid in execution, and likely cost-effective compared to existing soil analytical labs. For example, each individual test strip costs $1.60 and the portable reflectometer costs approximately $1,000. In addition to the conditions mentioned, successful adoption requires training to increase awareness

of the potential benefits of the technology and hands-on training for proper execution of the SNQT protocols. Throughout my research program, I engaged directly with current CTAHR crop extension faculty and provided them with hands-on training on the correct implementation of the SNQT. As a result of this interaction, they are currently using the technology to improve N management for their respective clientele.

This research project provides a critically important first step in the adaptation process of the N management component of CropManage to Hawaii's unique environment and cropping systems. At this point, it is reasonable to use the CropManage algorithm (EQN 1.2) with the accompanying crop N uptake curve and residue N estimates (Appendix X) and the current NO_3-N critical concentration to guide N fertilization of napa cabbage on an Oxisol. To expand the cover of CropManage, the next phase of research needs to address the following: 1) expand napa crop and soil critical concentration datasets to Mollisols, Vertisols, and Andisols at locations on Oahu, Mauo, and Hawaii Islands. 2) branch out to other important vegetable crops (head cabbage, broccoli, sweet onion, lettuces and other greens, sweet and seed corn, and melons) across the same soil types, and 3) implement a comprehensive outreach and training program.

Appendix

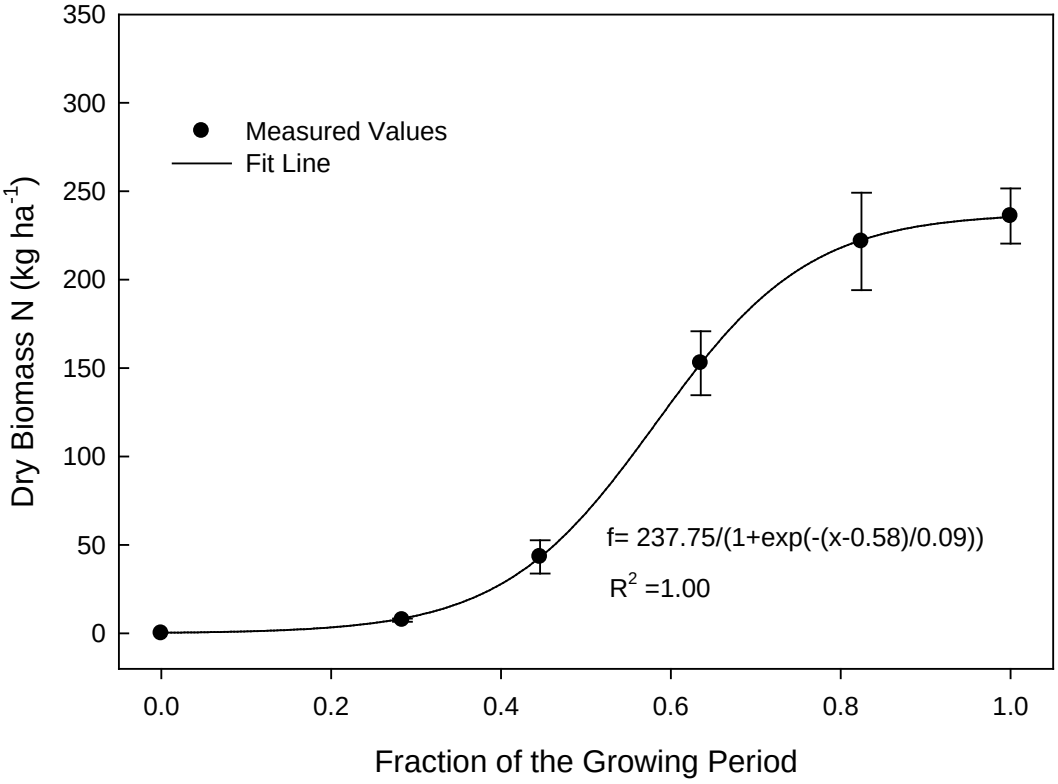
The following data was collected during on-farm activities to evaluate crop N uptake in conjunction to commercial practices representative of Hawaii vegetable farmers. The crops being presented were grown during the summer of 2016 between the months of June through August. The farm site was located in the Helemano area of Central Oahu on the Wahiawa soil series (Very-fine, kaolinitic, isohyperthermic Rhodic Haplustox). Crop data was used to model the patterns of N uptake dynamics and support key findings from our experiments discussed in this manuscript.

Modeling procedure

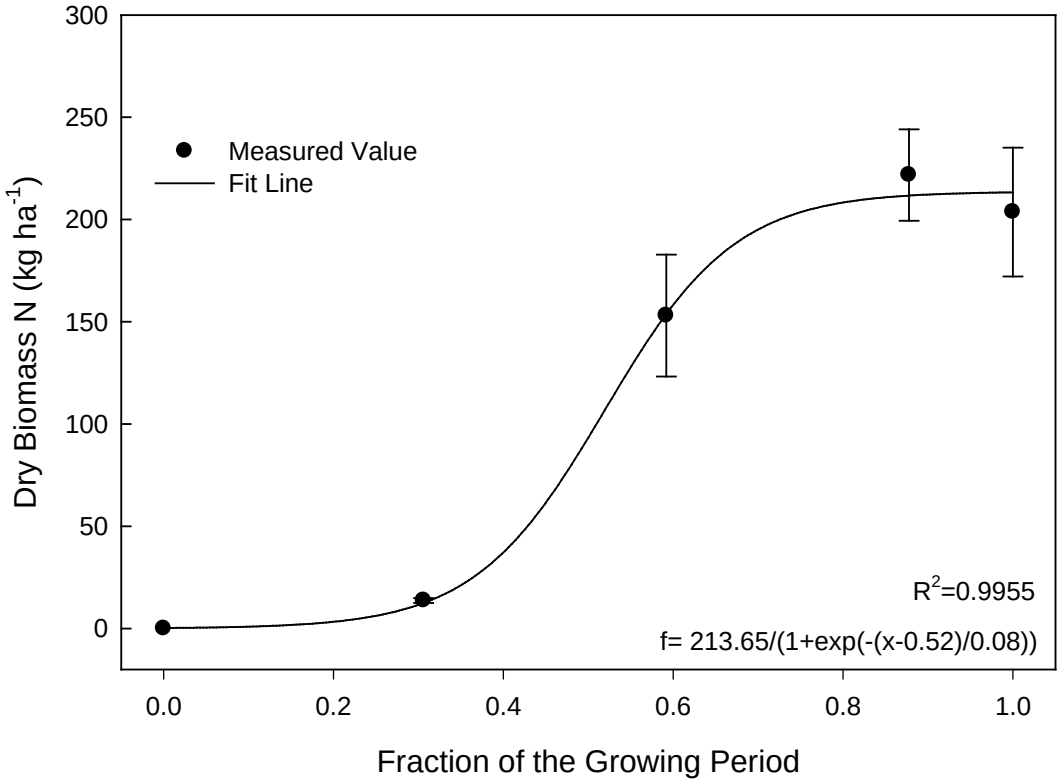
We used Non-linear regression analysis to model plant nitrogen uptake (PNU) over time using a three parameter sigmoidal curve in SigmaPlot (Systat Software, Inc., San Jose,CA) (see EQN. A.1)

$$f = \frac{a}{(1+\exp\left(\frac{-(x-x_0)}{b}\right))} \qquad \text{[EQN. A.1.]}$$

where f is the predicted crop N uptake, *a* is the crop N uptake asymptote (kg ha^{-1}) , *x* is the fraction of the growing period corresponding to each data point, x_0 is the inflection point, and b is the y intercept. The significance is that *a* is the predicted target yield and x_0 is the time in which the rate of N accumulation ceases to increase and begins to decrease. This is the point at which the rate of N absorption is the greatest.



Appendix Figure 1. Dry biomass N accumulation of head cabbage as a function of time within the growing period. Crop grown in the summer of 2016 on a commercial farm in the Helemano area of Central Oahu.



Appendix Figure 2. Dry biomass N accumulation of napa cabbage as a function of time within the growing period. Crop grown in the summer of 2016 on a commercial farm in the Helemano area of Central Oahu.

Appendix Table 1. Model parameters (see equation A.1.) describing the pattern of N uptake in head cabbage (*Brassica oleracea var.capitata*) and napa cabbage (*Brassica rapa subsp. pekinensis var.Yuki F1 hybrid*).

Crop	Field site	Planting Date	Fertilizer N (kg ha^{-1})	Days to harvest	x_0	x_0 Corresponding DAP	*b*	Crop N accumulation (kg ha^{-1})	
								Measured value	Predicted value (*a*)
Head cabbage	Helemano	5/21/2016	272	74	0.58	42.92	0.09	236	237.75
Napa cabbage	Helemano	6/1/2016	221	49	0.52	25.48	0.08	204	213.65

Data presented serves to illustrate the contrast in crop duration (Days to Harvest) and time corresponding to the maximum rate of N uptake (X_0) despite similarities in predicted crop N accumulation (a).

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